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AMBIENT TEMPERATURE BINDER CURE CATALYSTS
FOR HYDROXY TERMINATED SYSTEMS

By

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AUG 20 1970

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FOREWORD

Prepared by: Approved by:

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ABSTRACT

Numerous cure failures have been encountered in the search for catalysts which will provide ambient temperature cures for hydroxy terminated polybutadiene propellants. These cure failures have been found to be due to side reactions which affect the stoichiometry of the reacting species and play a more dominant role than higher cure temperatures. The two most important side reactions which can lead to cure failure and/or degraded mechanical properties are the moisture-isocyanate reaction and isocyanate-homopolymerization. Both of these reactions are accelerated by metal catalysts. Tetravalent alkyltin-salts like dibutyltindilaurate and dibutyl-tindiacetate accelerate the moisture reaction approximately ten times more than $Fe(AA)_3$ in uncatalyzed mixtures of the reactants, while the urethane reaction is accelerated more efficiently by metal catalysts.

Divalent tin, lead and copper derivatives were found to be the strongest homopolymerization catalysts. With the exception of Cu-compounds this homo-polymerization is strongly suppressed by ammonium perchlorate. A potential cure system using isocyanate trimerization as a crosslinking reaction has been abandoned because of extremely poor mechanical properties.

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GLOSSARY

(AA)	Acetylacetonate
(Ac)	Acetate
B-2000	A poly(1,2-butylene-oxide)diol (mw $\cong$ 2000)
Bu	Butyl
BuOH	n-butyl alcohol
E	Young's modulus
$\dot{\varepsilon}$	Strain rate
ε_m	Elongation at maximum stress
ε_b	Elongation at break
HDI	Hexane diisocyanate
HTPB	Hydroxy terminated polybutadiene
IDP	Isodecyl pelargonate
k_2	Second order rate constant
MeOH	Methyl alcohol
Naph	Naphthenate
Neozone D	Phenyl-β-naphthylamine
Oct	Octoate
PPG	Polypropylene glycol (mw $\cong$ 2000)
R-45	A hydroxy terminated polybutadiene with primary functional groups, marketed by the Arco Chemical Co.
Thermolite T-12	Dibutyltin dilaurate
σ_m	Maximum stress
TP-4040	A trifunctional polypropylene glycol (mw $\cong$ 4000)
v_2	Gel fraction

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AMBIENT TEMPERATURE BINDER CURE CATALYSTS
FOR HYDROXY TERMINATED SYSTEMS

I.   INTRODUCTION

This is the second quarterly Technical Report submitted in partial
fulfillment of the requirements of Contract FO-4611-70-C-0017. This report
covers the period of 1 April 1970 to 30 June 1970.

Urethane propellants are normally cured at temperatures of 110-135°F.
A reduction of the cure temperature to 70-80°F would significantly reduce
propellant bore strains and bond stresses in case-bonded solid rocket motors.
The lower cure temperature could also result in better propellant mechanical
behavior, because side reactions are also minimized at lower temperatures.
Ambient temperature curing is doubly important for propellants containing
energetic fuels for binder components, which may decompose during cure at
higher temperatures.

II.   OBJECTIVE

The objective of this program is the development of catalysts which
promote the isocyanate-hydroxy reaction at room temperature under the con-
ditions expected in a solid propellant environment and to demonstrate the
effectiveness of these catalysts. This objective must be achieved without
seriously affecting propellant processing characteristics, mechanical he-
havior and storage stability. Primary emphasis is on systems where the
casting and curing operations are within 5°F. While modified catalysts are
being considered, principal emphasis is on commercially available catalysts.
The Milestone Chart for the program is shown in Figure 1.

III.   SUMMARY

A simplified analysis of cure-failure is given with the aid of which
maximum allowable impurity levels may be calculated. The moisture-
isocyanate reaction has been further explored, and the relative efficiency
of a number of metal catalysts for this reaction was ascertained. $Fe(AA)_3$,
Pb-octoate, Pb-naphthenate and Sn-octoate were found to be weak catalysts
for the moisture-isocyanate reaction, while the tetravalent tin salts like
dibutyltindilaurate (T-12) and dibutyltindiacetate are quite efficient.

The effect of temperature on the uncatalyzed as well as the
catalyzed $(Fe(AA)_3$, T-12) urea reaction with both HDI and TDI was ascer-
tained and found to be significantly greater for HDI.

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MILESTONE SCHEDULE

	Month of Program		
	1970	1971	
Task	J F M A M J J A S O N D	J F M A M J	
I. Phase I – Catalyst Behavior with Components of Composite Systems			
1. Catalyst Screening	X————X		
2. Gumstock Studies	X———X———X		
3. Model Compound Studies and One-lb Propellant Preparation	X———X		
4. Catalyst Modification	X————————X		
II. Phase II – Scale-up to 10-lb Batches			
1. Uncontaminated Propellants	X—————————X		
2. Propellants with Con-taminants	X————X———X		
3. Aging	X—————————————X		
4. Alternate Hydroxy Prepolymer Propellants		X———X	

Figure 1

-2-
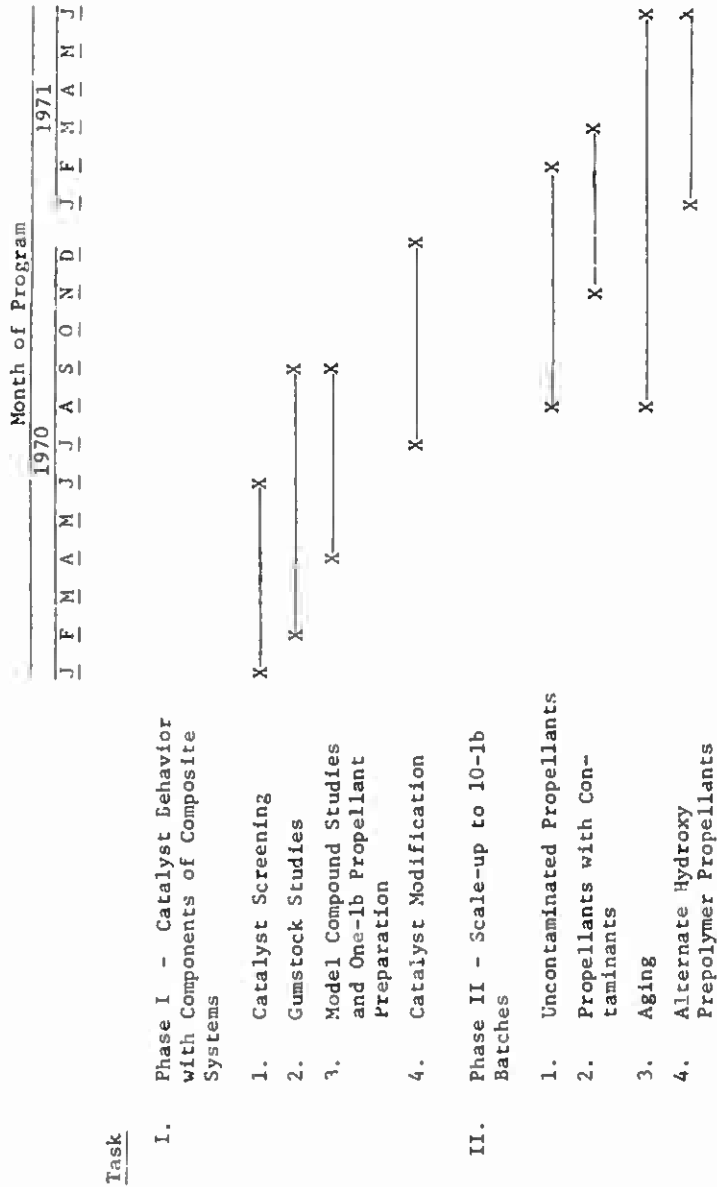
Catalysts preferentially boost the urethane reaction. Uncatalyzed, the urea reaction actually is slightly faster than the urethane reaction.

Homopolymerization of isocyanate is probably the second most important cause of cure-failure. It is strongly accelerated by many metal catalysts. Particularly detrimental are divalent tin- and lead-compounds and copper derivatives.

Trimerization of the isocyanate groups appears to be the dominant reaction as ascertained from homopolymerizations of phenylisocyanate and butylisocyanate.

Investigation of a potential cure system using trimerization of excess NCO-groups as a crosslinking reaction has been terminated because of very poor mechanical properties of the resulting propellants. Also a large variety of interference effects on homopolymerization, caused by minute changes of the environment, make this system unattractive.

Dry, dissolved ammonium perchlorate slows the rate of the $Fe(AA)_3$ catalyzed PPG reaction, but otherwise appears not to affect the final extent of cure. Ammonium perchlorate inhibits trimerization of TDI or HDI brought about by Pb- and tin-catalysts, but not the trimerization of HDI catalyzed by Cu-compounds.

IV. TECHNICAL DISCUSSION

A. INTRODUCTION

In the first quarterly report a large number of commercially available metal catalysts* have been screened for potential use in polyurethane propellants. Only a comparatively small number of the compounds were found to produce reliable cures at ambient temperature in typical propellant formulations. These compounds were: Ferric acetylacetonate, copper acetylacetonate, lead naphthenate and octoate and di- and tetravalent tin compounds. Copper acetylacetonate apparently promotes a different type of cure reaction if aliphatic diisocyanates are used. This becomes apparent from entirely different, generally very poor (i.e. weak and brittle) mechanical properties.

Obviously, failure of cure indicates that the stoichiometry of the hydroxyl-isocyanate reaction has been disturbed usually resulting in left-over hydroxyl groups. In terms of cure or mechanical properties this means dangling unconnected chain ends whose effect on physical properties

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*Base catalysts like N-alkyl morpholines, trialkylamines, and bridge-head nitrogen compounds (e.g. DABCO = triethylenediamine) have been omitted in these studies because of their obvious incompatibility with ammonium perchlorate.

is two fold, namely a reduction of the quantity of load bearing structure
leading to mechanically weak propellants, and secondly an effective re-
duction of crosslink density which is the primary source of cure failure.
The fact that $Fe(AA)_3$ and some of the other catalysts generally promote
cure does not necessarily indicate that the cure reaction proceeds 100
per cent in the desired direction, it only indicates that less of the
isocyanate-consuming side reactions occur. It is clear that in order to
obtain optimum properties such side reactions should be avoided or brought
under control. This second quarterly report, therefore, has been devoted
to the elucidation and more quantitative exploration of the two most
important sources of cure failure, i.e., the moisture interference reaction
and consumption of isocyanate by homopolymerization, so that corrective
action may be taken.

B.   THEORETICAL ESTIMATION OF THE LEVEL OF SIDE REACTIONS
     WHICH MAY CAUSE CURE FAILURE

Experience has shown that in order to obtain propellant cures
a crosslink density of about 5×10^{-5} moles of trifunctional branch points
per gram rubber matrix (corresponding to about 7×10^{-5} moles chains/cm^3 in
a FBD matrix) is required. Usually this value is somewhat higher for pro-
pellants with a low solids loading (below 84 weight %), and lower for highly
loaded propellants.

In ideal propellant binder matrices all individual prepolymer
chains are hooked together at their ends, so that there are no dangling,
unconnected chain ends. If crosslinking is obtained through incorporation
of trifunctional compounds, the theoretical crosslink density, ν_{th} expressed
in moles chains per cm^3 is given by:

$$\nu_{th} = \frac{3d}{2} \sum_{i-1} \frac{n(f_i - 2)}{f_i} \frac{W_i}{E_i} \tag{1}$$

where, d is the density of the rubber, f_i is the functionality of the ith
component in the binder and may assume values between 1 and 3*, W_i is its
weight fraction, and E_i is the analytically determined equivalent weight.
The equation is based on the following considerations. Of an f-functional
compound two functions are used for chain propagation. Therefore, $(f-2)/f$

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*This equation does not necessarily hold for higher than tri-functional
crosalinkers. For the latter, several other definitions are also used.

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represents the fraction of the functional groups which is available for crosslinking. The crosslink density will be proportional to the weight fraction of the particular component and inversely proportional to its equivalent weight. Only those prepolymers with a functionality other than 2 contribute to the over-all crosslink density. Plasticizers ($f=0$) are excluded since they are not part of the rubber network. Their effect on mechanical properties and apparent crosslink density has been treated elsewhere (1). The factor $3d/2$ converts the crosslink density from "moles branch points/gram" to the more familiar "moles chains/cc".

If only a single trifunctional compound is used as the crosslinker, equation 1 reduces to

$$\nu_{th} = (d/2)(W/E), \tag{2}$$

or if the crosslink density is expressed in terms of moles branch points/ gram

$$\nu_{th}' = W/M \tag{2'}$$

where M is the molecular weight of the trifunctional compound.

Homopolymerization as well as moisture interference (urea-formation) will consume isocyanate. This isocyanate will be lacking for completing the cure reaction, so that the net effect is chain termination. Neither the moisture reaction nor homopolymerization (trimerization) per se will produce unconnected chain ends, since one mole of water will always react with two equivalents isocyanate to form one urea linkage, and tri-merization consumes three equivalents NCO to form one crosslink. The point is that the quantity of isocyanate thus consumed will vary depending on the environmental conditions and cannot be readily accounted for in the calcu-lation of the required quantity of diisocyanate in a propellant formulation. The effect of insufficient isocyanate on crosslink density for the case of small levels of termination can be calculated from equation 1 which takes the form

$$\nu_t = -\frac{3d}{2} \frac{\Delta W_{DI}}{E_{DI}} \tag{3}$$

where ΔW_{DI} is the difference between the stoichiometrically required weight fraction of diisocyanate and the actual weight fraction. Each isocyanate group of the diisocyanate missing from the stoichiometric quantity will leave one unconnected chain end. Therefore ν_t is a negative increment, which has to be deducted from the overall crosslink density. For every urea

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linkage formed one crosslink is destroyed and for every trimer crosslink, three other crosslinks will not be formed, if one started with stoichiometric quantities of hydroxyl and isocysnate groups. This somewhat oversimplified trestment considers only the effect which chain termination will have on cure, it does not account for its effect on mechanical properties. Chain termination always is accompanied by a profound worsening of properties with respect to strain and stress capability of rubbers or propellants. A more detailed treatment has been given elsewhere (2).

Two simple cases may be considered to demonstrate the effect of side reactions on the overall propellant cure. Assume the theoretical crosslink density $\nu_{th}' = 5 \times 10^{-5}$ moles branch points/g. Hence in 100g of a 88 wt% loaded propellant there are 6×10^{-4} moles branch points. In order to neutralize these, an equal molar quantity of chain terminator is required. In case of moisture interference (since one moles of water consumes two equivalents isocysnate) $9 \times 6 \times 10^{-4} = 0.0054$g H_2O/100g propellant are required. This quantity is just slightly above the surface moisture content of oxidizer stored with bags of drying agents (usually surface moisture of unground AP is between 0.002 and 0.003%). At present it is not known to what extent this moisture will enter into the cure reaction. Tests to determine this are presently being conducted.

In the second case we want to find out what percentage of the isocyanate of the propellant batch, if trimerized[*], will suffice to offset crosslinking. Here three NCO-groups will be removed and one crosslink formed. The simplified net effect is two terminations per three trimerizing NCO-groups. Hence, for the above case $(3/2) \times 84 \times 6 \times 10^{-4} = 7.6 \times 10^{-2}$ grams of HDI must trimerize to cause cure failure. The level of HDI in such propellants is around 0.5%, therefore if $0.076/0.5 = 15$ percent of the HDI trimerizes cure failure may occur if no provision for such an effect are taken. It will be shown later that the magnitude of such effects are easily within the range of encountered homopolymerization. Thus moisture effects and isocyanate selfcondensstion reactions can readily account for the observed cure failures.

In general, a slight excess of NCO over OH is used to account for such reactions. In well curing systems, excess isocysnate may, however, result in additional crosslinking as a result of trimerization. In fact, in a concurrent program (3) it has been observed that no crosslinking agent is needed in a difunctional HTPB binder cured with either HDI or TDI only. It is not known at present whether this cure is due to NCO-trimerization or a yet unknown reaction. It definitely is no artifact. Propellants were made with these binders and their equilibrium swelling properties were ascertained. It is clear that to obtain good cures and, equally important, acceptsble mechanical properties, it is mandatory that these side-reactions be elucidated and be brought under control.

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[*]Trimerization is the most likely isocyanate selfcondensation reaction.

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C.   MOISTURE INTERFERENCE REACTION

During the first phase screening program a large number of catalysts were tested and found to be unsatisfactory* in that the propellant either failed to cure or cured incompletely. In many cases preliminary evidence pointed towards moisture interference. Therefore, a more detailed investigation of the moisture-isocyanate reaction has been initiated and is described below.

1.   General Considerations

The H_2O-RNCO reaction is probably the most important single cause for cure failure. The reaction proceeds via the very unstable carbonic acid, viz

$$RNCO + H_2O \rightarrow [RNHCOOH] \rightarrow RNH_2 + CO_2$$

which decomposes to amine and CO_2. The amine* immediately reacts with a second molecule of isocyanate to form the stable end-product urea. Thus the net reaction is

$$2RNCO + H_2O \rightarrow RNH-CO-NHR + CO_2$$

If the water could be quantitatively reacted the propellant would cure, since only the introduction of additional urea linkages for every molecule of water reacted occurs, e.g.,

$$...-CH_2OCONH-(CH_2)_6-NCO + H_2O + OCN-(CH_2)_6-NHCOO-CH_2-...$$

$$...-CH_2-OCONH(CH_2)_6-NH-CO-NH-(CH_2)_6-NHCOO-CH_2-...+CO_2$$
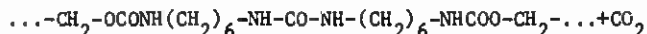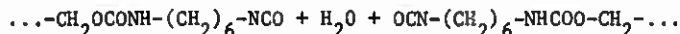
The exact amount of water in a propellant is usually not known but may become appreciable and in some binder systems resulting substantial CO_2-evolution. In HTPB binders, moisture poses less of a problem than in polyethers because of the infinitesimal solubility of H_2O in the hydrocarbons. However, as shown above, it takes only minute quantities of H_2O to significantly affect the cure stoichiometry.

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*Aliphatic amines and amines having aromatic skeletons which are not substituted by electronegative groups ($-NO_2$, F) will react much faster than OH with isocyanate. This is in accord with the fact that no free amine is detected in such reactions regardless of the NCO/H_2O ratio. However in amines where the basicity of the NH_2-group is reduced by electronegative substituents, this is no longer the case (4) and chain termination may result.

2. Catalysis of Moisture Reaction

The moisture reaction appears to be catalyzed by the same catalysts which accelerate the urethane reaction. Some metal catalysts appear to be hydrolyzed and are thus inactivated by water. The metal octoates and naphthenates are especially susceptible, while dibutyltin salts appear to be the most stable towards hydrolysis. An indication of catalyst degradation may be the decline of catalytic activity during the course of the reaction. For example, dibutyltindilaurate is initially less efficient than uranylacetylacetonate but soon becomes more effective as the reaction proceeds (Figure 2).

Table 1 lists the relative efficiency of many metal catalysts for the water reaction with HDI carried out in acetone. Dioxane was found unsuitable for this study since an interference of unknown nature occurs. Because order and molecularity of the isocyanate-water reaction are unknown rate data are listed in terms of percent of the HDI reacted rather than some rate constant, which depends on the chosen mechanism.

In many instances, the catalyst was not completely soluble or a precipitate formed as a result of partial hydrolysis by the water. Notably the octoates and naphthenates are susceptible to hydrolysis. Extrapolation of these data to other concentrations and environments are of questionable value, because of the complexity of the water-NCO reaction which probably exceeds that of the urethane reaction.

Since none of the octoates and naphthenates were completely soluble in acetone containing 2% water, additional studies were conducted with MEK and ethylacetate solution which contained only 1% water. Even here most of the compounds were partially hydrolyzed, evident from the formation of a precipitate upon the addition of water. The results are shown in Table 2.

For comparative purposes, the catalyzed isocyanate-butanol reaction was also studied in acetone at the same molar concentration. After only 80 min. the reaction was essentially complete with $Fe(AA)_3$ and dibutyltindilaurate; with lead naphthenate, lead octoate, and tin octoate, the reactions were 31, 20 and 25 percent complete, respectively. Comparison of these results with those in Tables 1 and 2 shows that the urethane reaction is catalyzed much more effectively than the urea-reaction.

Figures 3 - 6 show time vs. conversion plots for the uncatalyzed and catalyzed water reaction. Figures 3 and 4 show that the H_2O-RNCO reaction in the uncatalyzed state is actually faster than the alcohol-isocyanate reaction for both HDI and TDI at ambient as well as elevated temperature. The reaction rates were obtained to ascertain the effect of temperature on the velocity of the reaction. As shown, the temperature effect is much stronger for HDI than TDI reactions, which finds its expression

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EFFECTIVE CATALYSTS ON THE WATER-HDI REACTION
(0.2% Catalyst) Acetone Solvent ($H_2O=1.1M$; HDI=0.23M; T=25°C)

Figure 2

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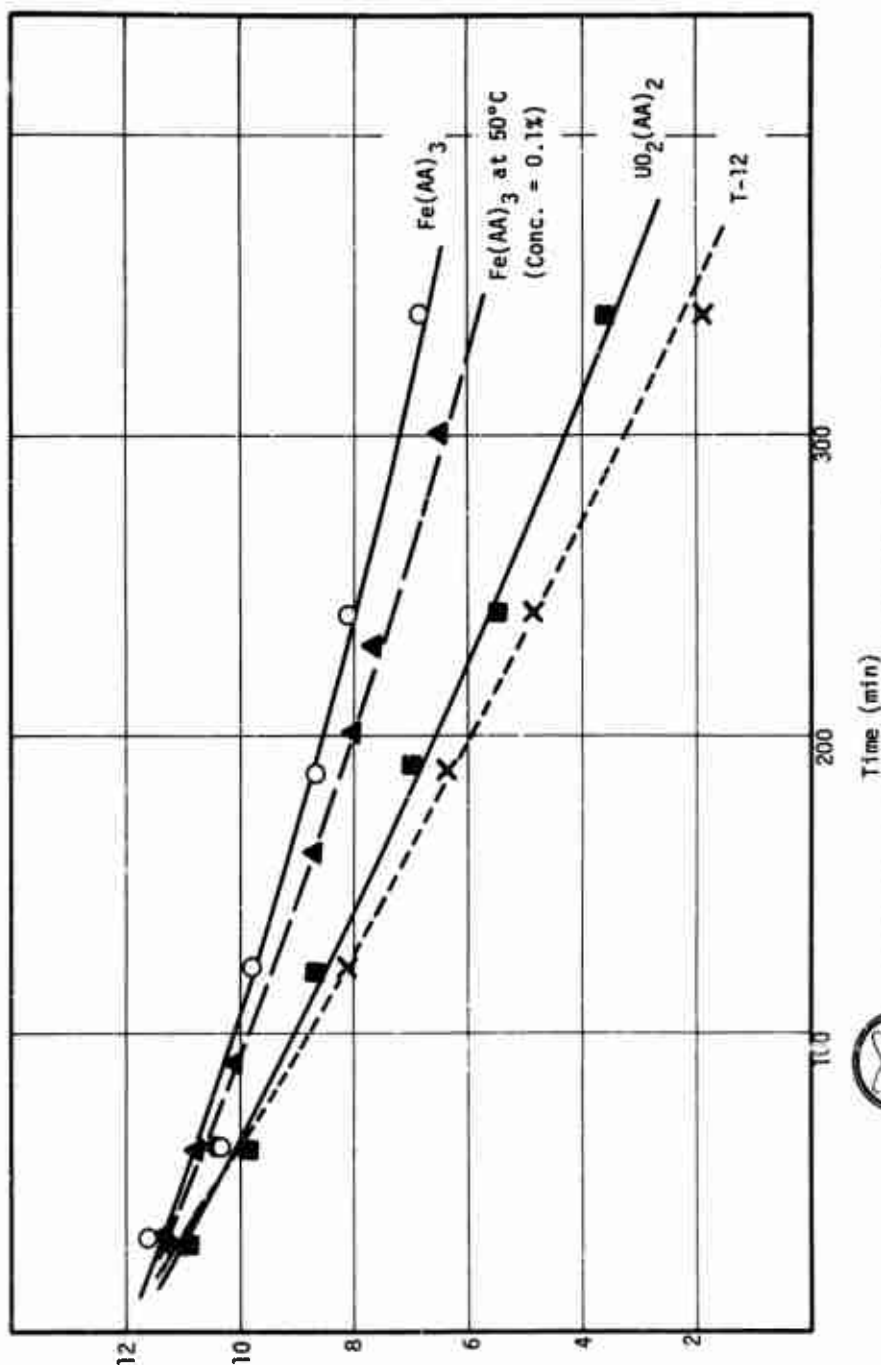
TABLE 1

RELATIVE EFFICIENCY OF METAL CATALYSTS FOR THE H_2O-HDI REACTION IN ACETONE[a] AT 25°C

Compound	HDI Reacted[b], %	Compound	HDI Reacted[b], %
$Fe(AA)_3$	38	$Cr(AA)_3$ (i)	10
$Mn(AA)_3$	38	$Co(AA)_3$ (i)	5
$Mn(AA)_2$ (i)	28	$Co(AA)_2$	21
$Cu(AA)_2$ (i)	33	$In(AA)_3$	28
Cu octoate	71	Ni-octoate (i)	19
$Th(AA)_4$	27	$Pb(AA)_2$ (i)	5
$Zr(AA)_4$	30	Pb naphthenate (i)	6
$Ce(AA)_4$ (i)	17	Pb octoate (i)	8
$Ce(AA)_3$ (i)	15	Sn-octoate (i)	19
$UO_2(AA)_2$	61	Bu_2 Sn laurate	53
$V(AA)_3$	26	Bu_2 Sn acetate	75
$VO(AA)_2$	32	Control 24 hrs	ca 3.5
$TiO(AA)_2$ (i)	28		
$Zn(AA)_2$ (i)	31		
Zn naphthenate (i)	23		
Zn decanoate (i)	24		
$Ni(AA)_2$	28		

(a) H_2O = 1.1M, HDI = 0.23M, catalyst ~ 0.4%; (b) = percent HDI reacted in 3 hrs; (i) not completely soluble or partial hydrolysis.

TABLE 2

RELATIVE EFFICIENCY OF SOME METAL-CATALYSTS FOR THE WATER - HDI REACTION[a] AT 25°C

	% NCO Reacted During 4 hrs in Solution of	
	MEK	Ethylacetate
Bu_2 Sn laurate	51	49
Zn naphthenate (P)	30	14
Zn decanoate (P)	26	9
Cd naphthenate (P)	10	9
Cu octoate	76	68
Sn octoate (P)	10	5
Pb octoate (P)	2	1
Pb naphthenate (P)	2	2

(a) $H_2O = 0.55M$, HDI = 0.23M; catalyst - 0.4%

(P) Catalyat precipitated upon addition of water.

UNCATALYZED REACTION BETWEEN TDI - BuOH AND TDI - H₂O

Figure 3

-12-
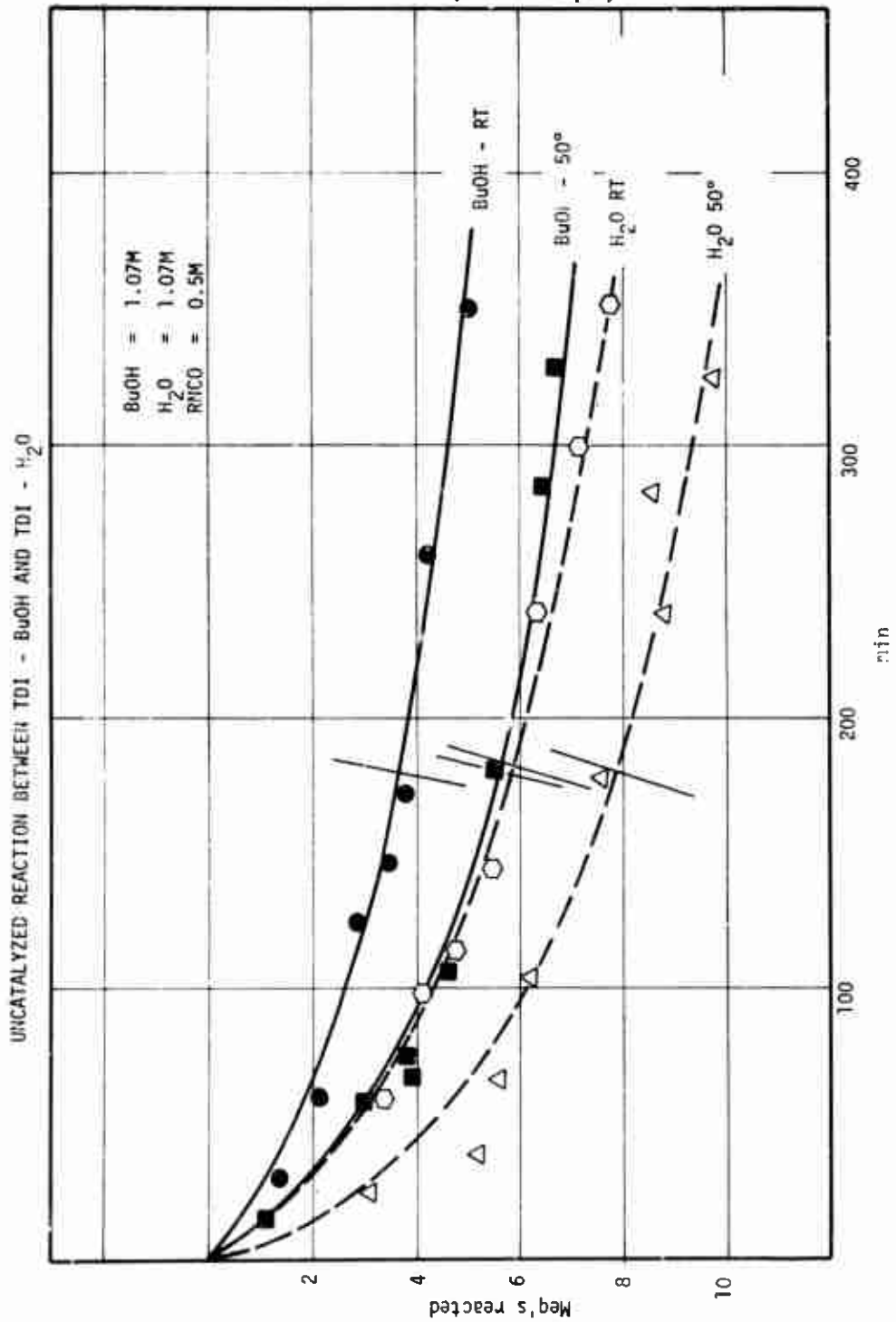
UNCATALYZED REACTION BETWEEN HDI - BuOH AND HDI - H_2O IN ACETONE

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Figure 4

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CATALYZED REACTION BETWEEN HDI AND H₂O IN ACETONE

H_2O = 1.07M
HDI = 0.5M
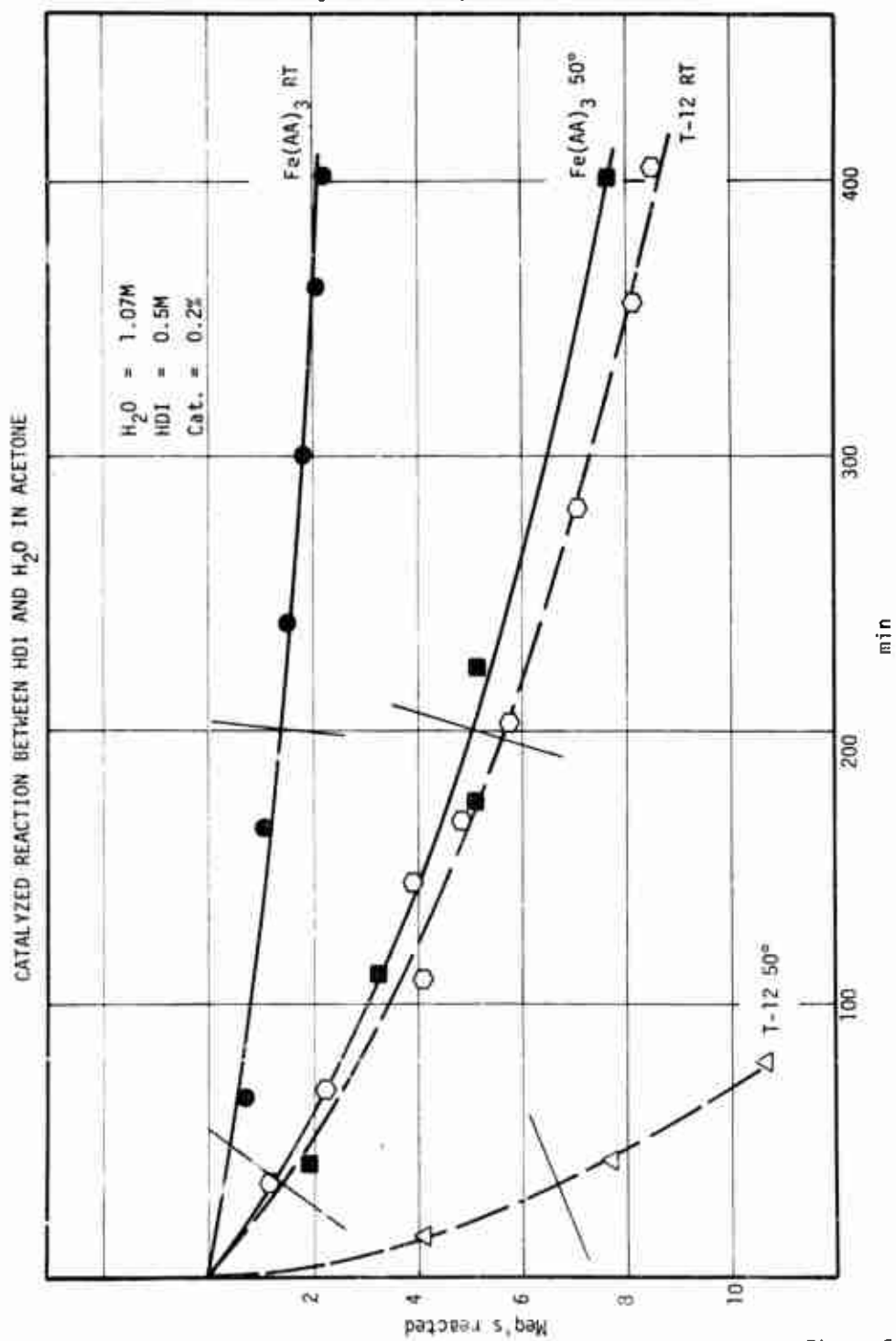Cat. = 0.2%

Fe(AA)₃ RT

Fe(AA)₃ 50°

T-12 RT

T-12 50°

Meq's reacted

min
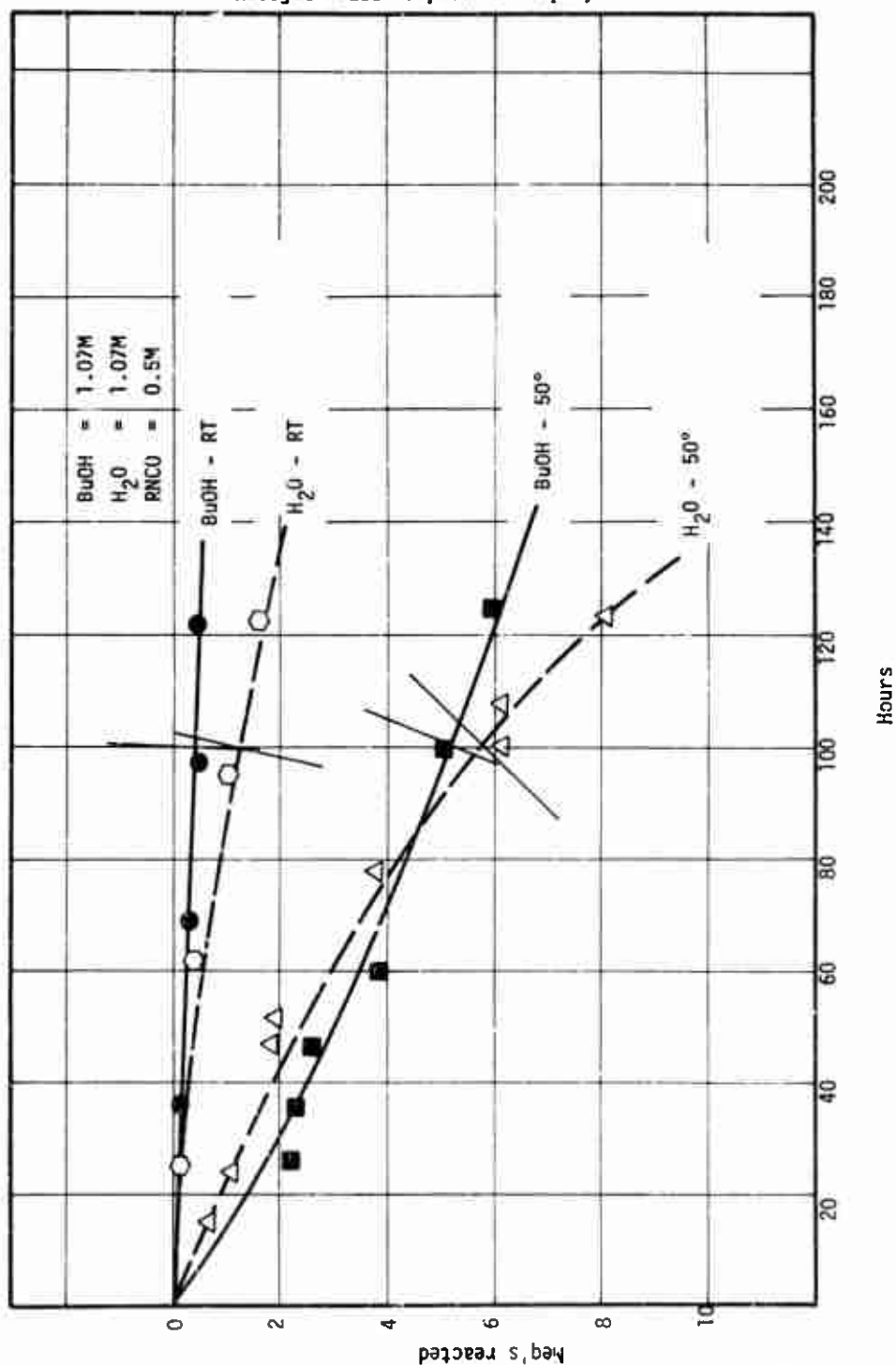
Figure 5

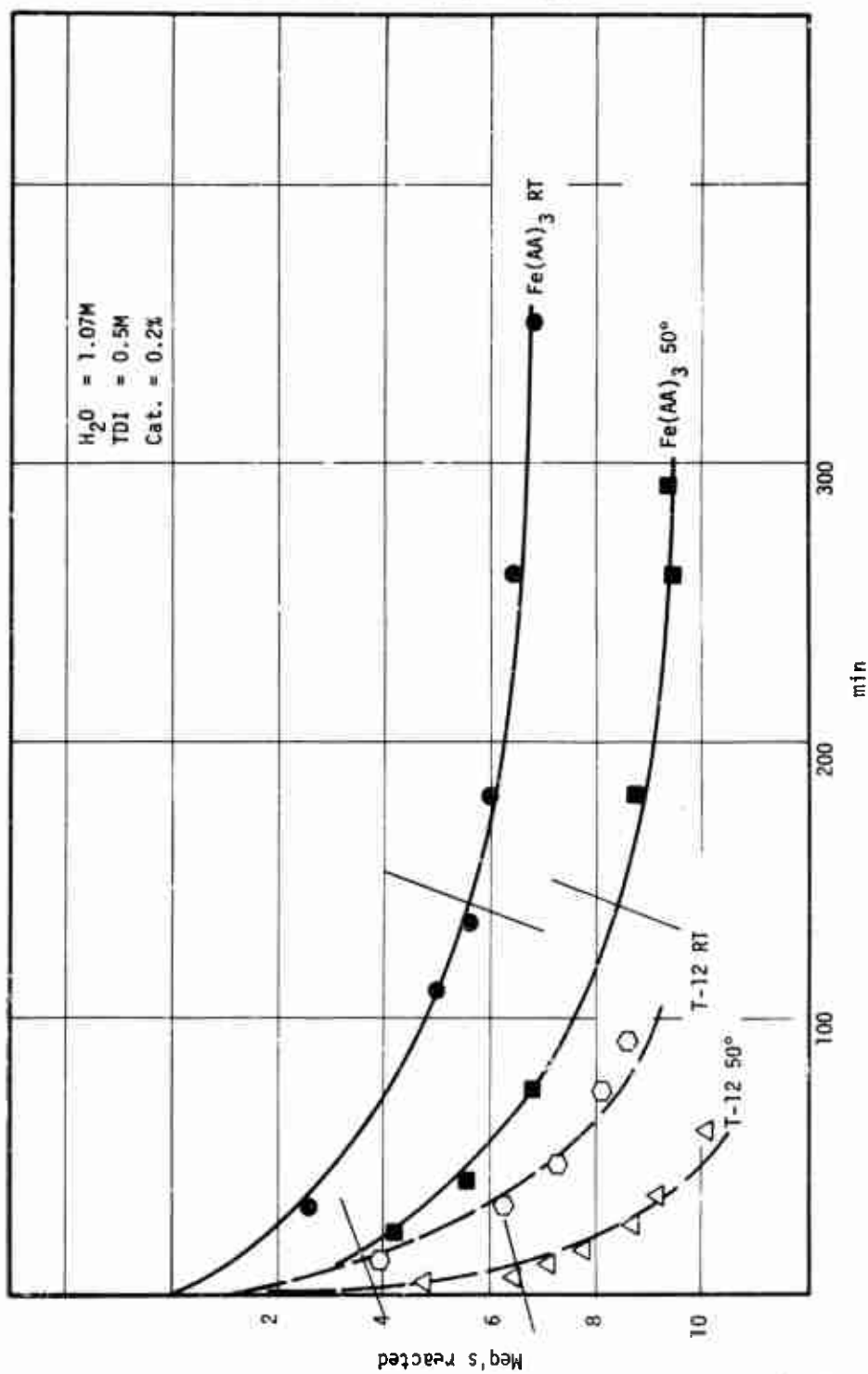CATALYZED REACTION BETWEEN TDI AND H₂O IN ACETONE

Figure 6

-15-

in the much higher activation energy. In order to obtain some sort of comparison between rates of the H_2O versus the velocity of the alcohol isocyanate reactions the apparent second order rate constants have been calculated from the graphs. The water-isocyanate reaction is certainly not second order (neither is the urethane reaction), but the first step in the reaction sequence:

$$RNCO + H_2O \rightleftharpoons [RNHCOOH] \rightarrow RNH_2 + CO_2$$

probably is second order. Since it is slow compared to the subsequent reaction:

$$RNH_2 + RNCO \rightarrow RNH-CO-NHR$$
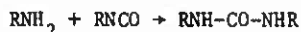
it will be rate determining. The rate constants so obtained depend somewhat on the location of the point on the curve* from which the rate constant was obtained. Considering the overall difficulty involved in obtaining these data, caution should be exercised in too much extrapolation. Nevertheless it is of interest to compare the rate constants with those found previously for the urethane reaction (5). A PPG/IDP/BuNCO mixture OH=NCO=0.63M, catalyzed with 0.4% T-12 (dibutyltindilaurate) or $Fe(AA)_3$ respectively, gave 14 and 21 x 10^{-3} E^{-1} min^{-1} for the two catalysts at 25°C. A R45/IDP/BuNCO mixture, OH=NCO=0.5M, catalyzed with o.2% of the tin- and iron catalyst, gave 18 and 17 x 10^{-3} E^{-1} min^{-1} respectively. Thus it appears that the urethane reaction catalyzed with $Fe(AA)_3$ is about 50 times faster than the H_2O reaction, while this ratio is much less favorable for T-12. Some cure failures observed with T-12 but not with $Fe(AA)_3$, may thus be explained.

The activation energies were calculated from the Arrhenius equation:

$$k = Ae^{-E/RT}$$

which for the rate constants at two temperatures takes the form:

$$\ln(k_1/k_2) = -(E/R)(1/T_1-1/T_2)$$

Introducing the values for R, T_1 and T_2:

$$E = \log (k_2/k_1)/5.7 \times 10^{-5} \text{ cal.}$$

Without knowledge of the true mechanism, it is difficult to define the activation energy of the reaction, thus activation energies calculated here are portraying essentially only the temperature dependence of the overall reaction. The activation energies calculated from the time-conversion curves shown in Figures 3 - 6 are

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* In order to obtain comparable values between the reaction velocities at the two temperatures, the rate constants were obtained at the same time. The point at which this was done is indicated by the short line on the curve, which is the normal to the tangent at that point. The normal was drawn by means of a mirror device.

listed in Table 3. The values in parentheaea are suspect because of the very alow converaion of the uncatalyzed HDI reactions which introduces great errors. It is readily observed that temperature changes affect HDI reactions much more than TDI reactions.

It may be mentioned that all rate data concerning the H_2O-RNCO reaction were obtained titrimetrically according to the method described in the previous quarterly report (6). Titrations were conducted electrometrically becauae of the heterogeneous nature of this reaction and the inherent difficulty in the titration (the polyurea is precipitated during titration as a sticky mass which tends to clog-up the electrodes. Addition of CCl_4 to the liquid prior to titration alleviates this problem somewhat by forming an emulaion with the polyurea). The reported valuea have a precision of probably no better than $\pm$ 20%. One should also bear in mind that many of the catalysts are decomposed during the reaction which further complicates the picture and makes meaningful data very difficult to obtain.

In conclusion it may be stated that with respect to cure failure, water is a moat likely culprit. The magniture of its effect on cure is lessened through catalysis, particularly with a suitable catalyst, because the urethane reaction is boosted more efficiently by the catalyst, than the urea reaction. The best catalysts for this purpose appear to be $Fe(AA)_3$, Pb-naphthenate, Pb-octoate and Sn-octoate. With the latter three it is not yet resolved whether poor hydrolytic stability, leading to inactivation of the catalyst, or truly poor efficiency towarda water catalysis is the governing factor. It is planned to prepare lead compounds with improved hydrolytic stability which may solve or at least shed more light on thia problem.

D.   HOMOPOLYMERIZATION OF ISOCYANATES

1.   Effect on Cure

Selfcondenaatiou of isocyanates is probably the second most important cause of cure failure particularly in HTPB-propellants where moisture interference, due to the infinitesimal solubility of water, ia a less likely course. A number of the more promising catalysts from the previous screening program were tested in a R45/IDP/TDI binder aystem loaded to 85 percent with AP and aluminum. In this test propeliant the necessary crosslink level can be adjuated by simply varying the concentration of the diisocyanate because the functionality of the HTPB-aystem is greater than two. The effect of HDI variations in such a system is shown below.

TDI wt%	Mechanical Properties at +77° F		
	o_m, psi	ε_m, %	E_o, psi
0.42	90	30.5	370
0.46	172	20.2	1100
0.50	194	14.3	1730

$\dot{\varepsilon} = 0.74$ in./in./min

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TABLE 3

ACTIVATION ENERGIES AND APPARENT SECOND ORDER RATE CONSTANTS
OF THE REACTIONS SHOWN IN FIGURES 3 - 6

|		$E(Kcal)$	$10^3 k [E^{-1} \ min^{-1}]$	
			$25°$	$50°$
BuOH/HDI	Uncatalyzed	(12)	0.0043	0.024
BuOH/TDI	Uncatalyzed	5.3	1.3	2.4
H_2O/HDI	Uncatalyzed	(8.5)	0.097	0.27
H_2O/TDI	Uncatalyzed	6.5	2.4	5.5
H_2O/HDI	$Fe(AA)_3$ 0.2%	15	0.35	2.5
H_2O/TDI	$Fe(AA)_3$ 0.2%	3.2	2.9	3.8
H_2O/HDI	T-12 0.2%	20	3.1	44
H_2O/TDI	T-12 0.2%	5.4	29	59

For the study of the other catalysts, a TDI level of 0.44% nnd a catalyst level of 0.005% was chosen. The catalysts tested included $Fe(AA)_3$ (control), Pb-naphthenate, Pb-octoate, $Pb(AA)_2$, Sn-octoate, dibutyltin-dilaurate, Zn-naphthenate, Ni-octoate and Cu-octoate. With the exception of the dibutyltindilaurate and the $Fe(AA)_3$ control, none of the catalysts gave satisfactory cure. All appeared to be deficient in isocyanate level and yielded very soft, undercured propellants.

The fact that T-12 catalyzed propellants cured strongly indicates that water-interference was probably not the cause of cure failure. Infrared studies on the benzene extract* of the uncured propellant showed no NCO-absorption, therefore incomplete reaction can be ruled out. In fact addition of more TDI brings about cure in all the propellants with all catalysts tested to date (7). While this correction of cure is possible in the case of R45 type HTPB propellants, it may not be so in systems with more difunctional prepolymers. Therefore it is important to gain more insight into the mechanism of this type of cure interference. This cure failure is most probably caused by homopolymerization of isocyanate.

2. Types of Self-Condensation Reactions

Self-condensation reactions of isocyanates can yield a variety of products, the most probable and well known ones being dimers, trimers and linear polymers, viz:

dimer   trimer   linear polymer
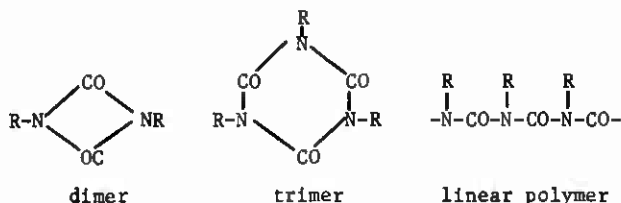
At high temperatures and with suitable catalysts carbodiimides (R-N=C=N-R) may result from the previously obtained dimer. Dimerization of aliphatic isocyanates is not known.

If dimerization and trimerization occur it is obvious that it may lead to cure failures due to NCO deficiency. For example, in case of dimer formation, four equivalents of NCO are required to react and link together two equivalents of OH. Thus for every dimer linkage formed two unconnected chains remain, i.e., in effect we obtain chain termination, if

*To obtain the benzene extract a quantity of the uncured propellant is digested with benzene. Solids are allowed to settle and the clear supernatant layer is decanted into an evaporating dish. Most of the benzene is evaporated in a vacuum oven. From the concentrated solution a smear is prepared whose IR spectrum is immediately obtained. Figure 4b shows such a spectrum.

a stoichiometric NCO/OH ratio was used initially. In the case of the trimer, one effective crosslink is formed from three equivalents of NCO, if the NCO groups stem from prepolymer chains, whose OH groups have reacted with a diisocyanate. Again, three OH groups must of necessity remain unreacted yielding three unconnected chain ends. As far as network formation is concerned one unreacted chain end just about neutralizes one trifunctional crosslink, so that the net effect of trimerization as well as dimerization is the reduction of the crosslink level, provided that the diisocyanate was not used in excess. The magnitude of the effect that this reaction has on the over-all crosslink density is shown in the first part of this report.

In the linear homopolymer, finally, every reacting NCO-group produces a branch-point and one residual OH group. Thus crosslinking and chain scission neutralize each other. But since urethane formation is in almost all cases considerably faster than self-polymerization, and because of a statistical distribution of the reacted species, there will be totally unreacted diols (serving as inert diluents in the network), and the net effect will be a very highly branched but very weak binder matrix. The type of condensation reaction occurring in the binder matrix should therefore be reflected in the mechanical properties of the cured product, as will be shown later.

3.   Catalysts for Self-Condensation Reactions

HDI and TDI self-condensations in toluene (10% solution) were conducted in sealed ampules. The content of the ampules were inspected periodically for evidence of gelation and/or precipitate. The results essentially corroborate those obtained earlier (8). The catalysts which did not cause either precipitation or gelation of TDI during 7 days ambient temperature storage followed by 2 days at 180° were: $Fe(AA)_3$, hexafluoro-acetylacetonate iron III, dibutyltindilaurate, $MoO_2(AA)_2$, $Th(AA)_4$, $Zr(AA)_4$, $Cr(AA)_3$, $Co(AA)_3$. Gels were produc | by Pb-octoate, Pb-naphthenate and Sn-octoate. All other catalysts yielded variable quantities of an insoluble precipitate. $TiO(AA)_2$, $V(AA)_3$ and $VO(AA)_2$ formed intensively dark solutions. In case of the HDI-toluene solution, gelation was effected by Pb-naphthenate, Pb-octoate, $Cu(AA)_2$, Cu-octoate, Sn-octoate, $In(AA)_3$, $V(AA)_3$, $VO(AA)_2$ and Zn-naphthenate. The latter four produced a gel only after the 180° storage. No marked change was found with $Fe(AA)_3$, dibutyltindilaurate $UO_2(AA)_2$, $Zr(AA)_4$, $Cr(AA)_3$ and $Co(AA)_3$. As with TDI, $TiO(AA)_2$, $V(AA)_3$ and $VO(AA)_2$ formed very dark solutions.

Butylisocyanate and phenylisocyanate were also subjected to homopolymerization reactions, because, being monomeric compounds, they yield well defined condensation products, and thus shed light on the products of homopolymerization brought about by the metal catalysts. In this case only the more potent catalysts for self-condensation; namely, Sn-octoate, Pb-octoate and naphthenate, Cu-octoate and $Cu(AA)_2$ were tested with pehnyl-isocyanate and butylisocyanate. The products of the condensation were found to be practically pure trimer. $Fe(AA)_3$ and T-12 were used as controls and
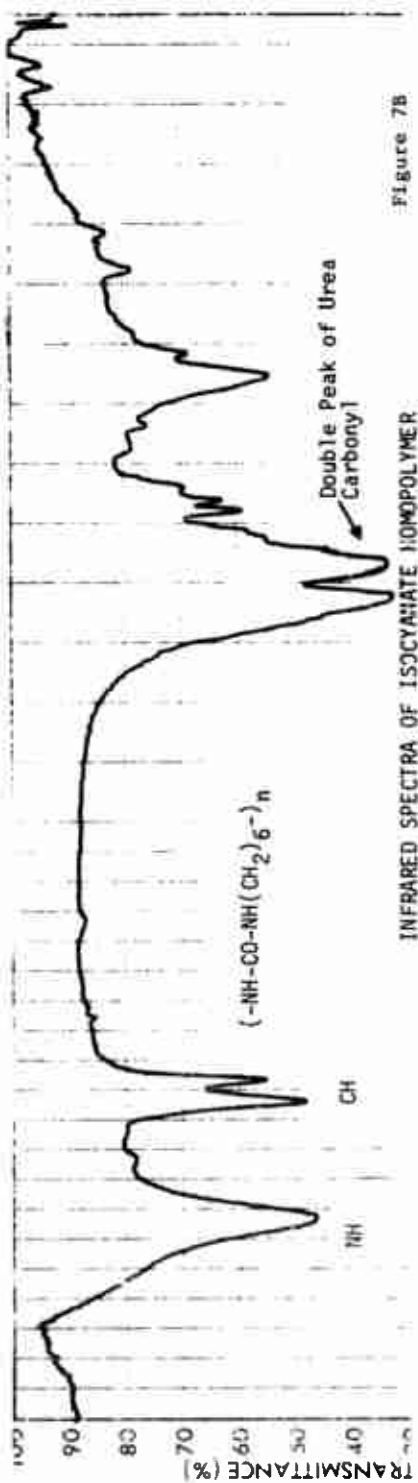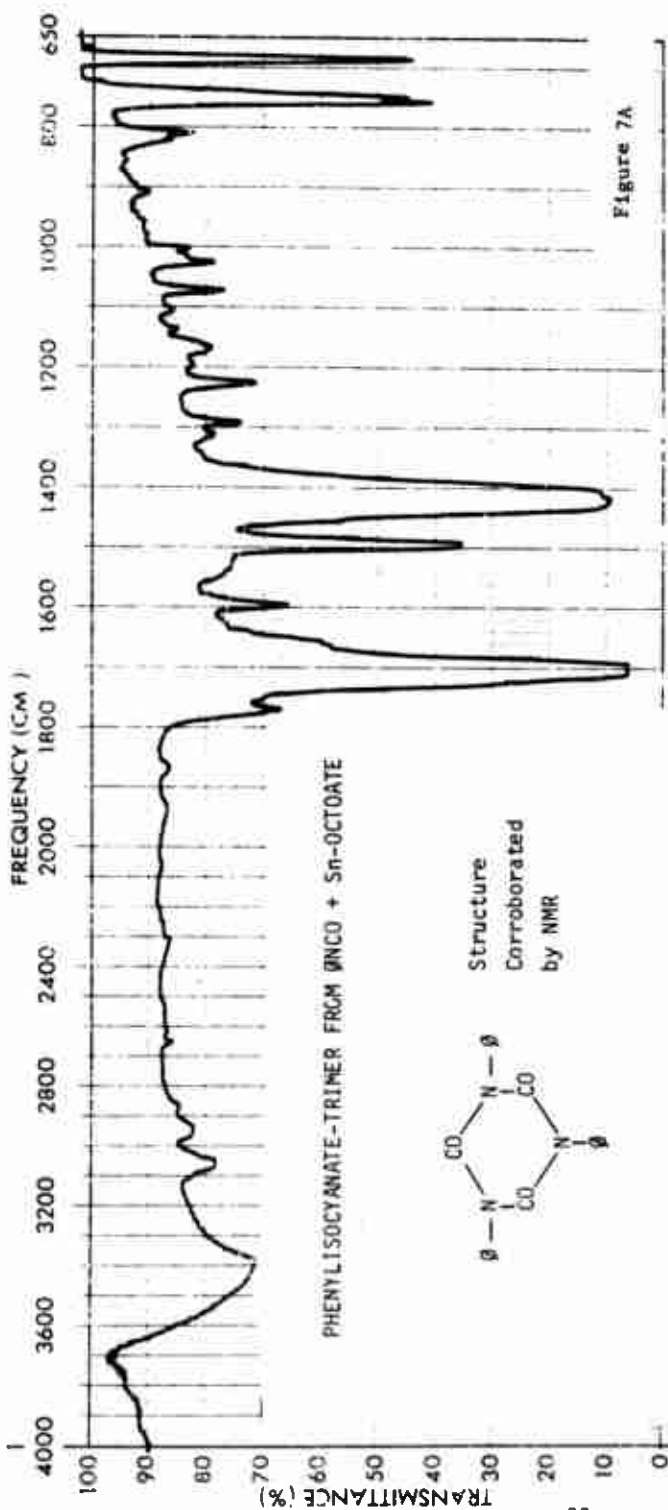
-20-

agsin proved rather ineffective in producing trimerization, as were the
copper compounds in case of the phenylisocyanate. The products were
identified by melting point, NMR, infrared and molecular weight deter-
minations. The tributylcyanurate is a high boiling liquid. Thus it appears
that these catalysts promote essentially trimerization reaction. Only in
the case of the Cu-compounds and aliphatic isocyanate formation of some
linear polymer may occur as indicated by a rather insoluble fraction and a
molecular weight somewhat higher than that corresponding to the trimer. In
the infrared spectrum of trimerized phenylisocyanate (Figure 7A) the peak
at 3400 cm^{-1} is difficult to explain, since in that region either O-H or
N-H stretching frequencies are involved. This grouping should not be present
in homopolymerized isocyanate. In an article (9) found in the literature,
claim is made that some urea groups are formed in the homopolymerization of
TDI which could explain this peak.

Figure 8A shows the infrared spectrum of the HDI-homopolymer
from $Cu(AA)_2$ in TEGDME, and Figure 8B the TDI homopolymer resulting from the
addition of stannous-octoate to pure TDI. The spectra are of little analytical
value, because of the absence of characteristic peaks. For comparative pur-
poses the infrared spectrum of a polyurea made from HDI and water is shown in
Figure 7B. The absence of the double peak of the urea carbonyl (Figure 7B)
rules out the suspicion, that the HDI-homopolymer may be mainly the result
of an accidential H_2O-HDI reaction. The most important infrared absorption
bands are summarized in Table 4.

It is interesting to note that $Cu(AA)_2$, which is very
active in bringing about homopolymerization of HDI appears to be much less
effective towards TDI. Homopolymerization is also effected by non-metallic
compounds. Tertiary amines both aromatic and aliphatic are well known, but
also some ethers were found in this study which also cause gelation of TDI,
particularly tetrahydrofurane. The solvents can augment the metal-catalyzed
homopolymerization very effectively. In some tests it was found that those
compounds conteining electron donor atoms (ether-oxygen and tertiary nitrogen)
are quite synergistic. For example, addition of Pb-naphthenate to a 10%
solution of TDI in dioxane or dimethylformamide caused a very strong exotherm.
The TDI solution containing Pb-naphthenate gelled within three days at ambient
temperature in the following solvents: ligroin, cyclohexane, carbon tetra-
chloride, dioxane and dimethyl formamide. MEK and butylacetate solutions
remained liquid, at least, during the first 10 days at room temperature.
Thus it may be anticipated that the backbone structure of the prepolymers
and plasticizers used in propellants will affect the cure reaction.

E.   INVESTIGATION OF A POTENTIAL CURE SYSTEM USING
     TRIMERIZATION AS CROSSLINKING REACTION

The reaction leading to cure may be depicted as follows:
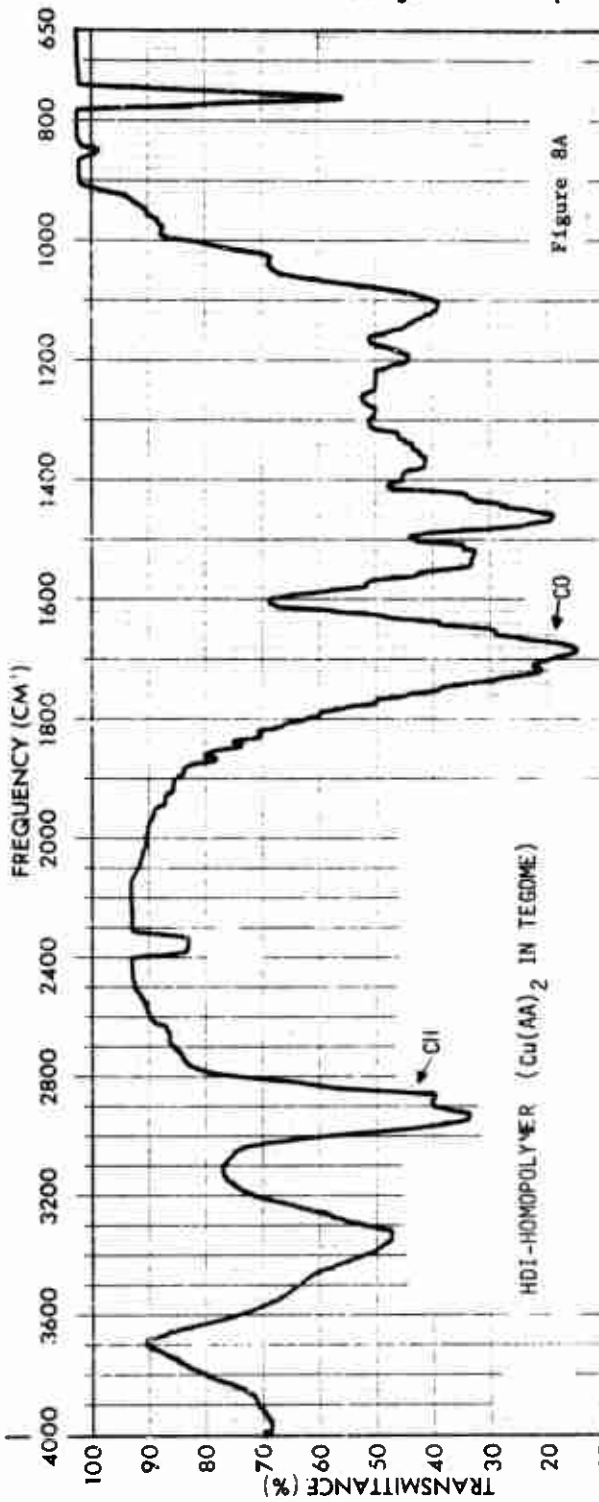
FREQUENCY (CM)
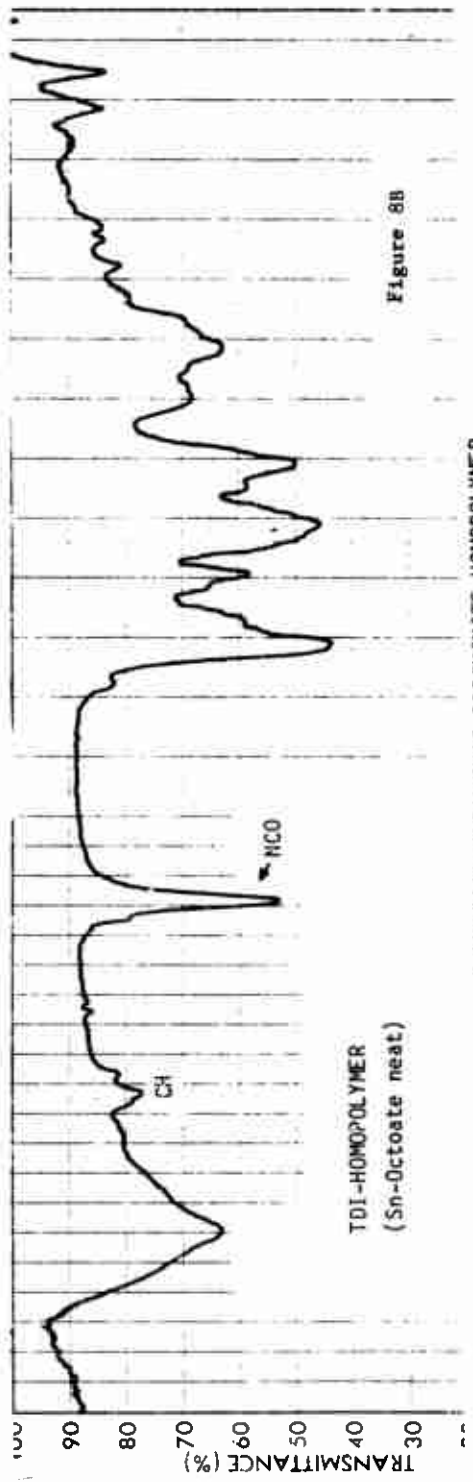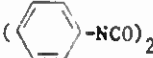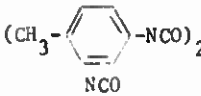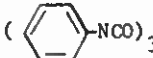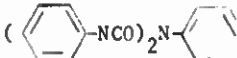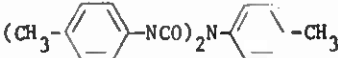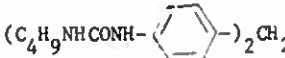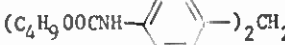
PHENYLISOCYANATE-TRIMER FROM ØNCO + Sn-OCTOATE

Structure
Corroborated
by NMR

Figure 7A

INFRARED SPECTRA OF ISOCYANATE HOMOPOLYMER

(-NH-CO-NH(CH$_2$)$_6$-)$_n$

Double Peak of Urea
Carbonyl

Figure 7B

CH

NH

TRANSMITTANCE (%)

TRANSMITTANCE (%)

INFRARED SPECTRA OF ISOCYANATE HOMOPOLYMER

Figure 8A

HDI-HOMOPOLYMER (Cu(AA)$_2$ IN TEGDME)

CO

CH

Figure 8B

TDI-HOMOPOLYMER (Sn-Octoate neat)

NCO

CH

FREQUENCY (CM^{-1})

TRANSMITTANCE (%)

TRANSMITTANCE (%)

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TABLE 4

INFRARED ABSORPTION SPECTRA OF MODEL COMPOUNDS IN KBr PELLETS

Compound	I R Bands, cm^{-1}				
A. Dimers					
$(C_6H_4-NCO)_2$	1780(s)[a,b]	1608(s)	1507(s)	1421(us)	
$(CH_3-C_6H_3(NCO)-NCO)_2$	1785(ms)[b]	1622(ms)	1515(s)	1387(s)	
$(CH_3-C_6H_3-NCO)_2$	2270(m)[c]	1775(m)[b]	1622(m)	1496(m)	1387(s)
8. Trimers					
$(C_6H_4-NCO)_3$	1780(m)	1708(s)[b]	1631(ms)	1496(ms)	1414(s)
$(CH_3-C_6H_3-NCO)_3$	1775(wm)	1710(s)[b]	1622(m)	1518(ms)	1408(s)
C. Biurets					
$(C_6H_4-NCO)_2N-C_6H_5$	1714(s)[b]	1675(m)	1594(ms)	1530(s)	1446(s)
	1315(m)	1262(m)	1225(m)	1182(m)	
$(CH_3-C_6H_4-NCO)_2N-C_6H_4-CH_3$	1714(s)[b]	1665(m)	1594(ms)	1514(s)	1403(m)
	1310(m)	1262(m)	1228(m)	1178(m)	1168(m)
D. Urea					
$(C_4H_9NHCONH-C_6H_4-)_2CH_2$	1642(s)[b]	1594(m)	1550(m)	1515(m)	1411(wm)
				1308(m)	1234(m)
E. Urethane					
$(C_4H_9OOCNH-C_6H_4-)_2CH_2$	1698(s)[b]	1616(m)	1530(s)	1416(m)	1340(m)
				1311(m)	1230(s)

(a) Intensities are designated qualitatively: w, wm, m, ms, s, us.

(b) Carbonyl stretching frequency.

(c) Isocyanate group.

$$3 \ R\text{-}OCONH\text{-}(CH_2)_6\text{-} NCO \rightarrow$$
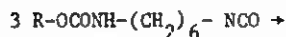
I

Where I denotes a prepolymer molecule reacted with hexamethylene diisocyanate. In order to obtain one crosslink three NCO-terminated prepolymer molecules have to be converted into the cyanurate-ring II. The quantity of additional NCO-needed to obtain the necessary crosslink density ν_{ch}, can be estimated from equation 1. Thus for a crosslink density of 5×10^{-5} moles branch points per gram of rubber, with no other crosslinker being used, the weight fraction of trimer (of HDI) is given by:
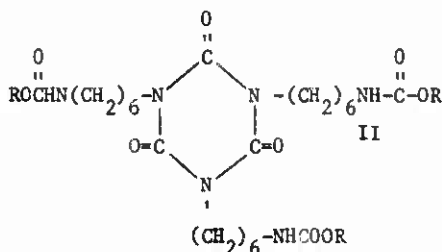
$$W_i = 3 \times 84 \times 5 \times 10^{-5} = 1.26 \times 10^{-2}$$

Hence 1.26% HDI is required over the amount necessary for the urethane reaction to produce the necessary crosslinking in the binder phase. For a typical propellant this quantity would reduce to about 0.1 to 0.2 percent, since propellants usually contain no more than 10-20% binder.

Table 5 shows some of the cures and the equivalent per cent isocyanate needed to obtain cure. About the same levels of isocyanate are needed if the B-2000 prepolymer is exchanged by HTPB's or other suitable prepolymers. Because of the obvious advantages that such a cure system offers (i.e. no separate crosslinker required) more work was devoted to the exploration of homopolymerization.

As reported previously lead naphthenate is best suited for TDI homopolymerization while $Cu(AA)_2$ is the most potent catalyst for HDI. Properties of binders prepared with B-2000 (a poly (1,2-butylene-oxide) diol) and excess HDI or TDI are compared in Table 6.

The mechanical properties obtained with the B-2000/HDI/$Cu(AA)_2$ binders are extremely poor and the B-2000/TDI/Pb-naphthenate binders are not much better. In both systems unconnected chain ends and an inherently

TABLE 5

CURE OF B-2000 WITH EXCESS TDI OR HDI USING
SELFCONDENSATION CATALYSTS
CURE 24 HRS AT 160°F

TDI Eq %	Sn-Octoate (0.5%)	Pb-naphthenate (0.5%)
103	No cure	No cure
115	No cure	Soft cure
126	Cure	Cure
137	Cure	Cure
150	Cure	Cure

HDI Eq %	Sn-Octoate (0.5%)	Pb-naphthenate (0.5%)	$Cu(AA)_2$ (0.5%)
83	No cure	No cure	No cure
95	No cure	No cure	Soft cure
107	No cure	No cure	Cure
119	Cure	Cure	Cure
131	Cure	Cure	Cure
143	Cure	Cure	Cure
155	Cure	Cure	Cure

TABLE 6

6a. MECHANICAL PROPERTIES OF B-2000/EXCESS HDI-BINDER CATALYST
(0.05% $Cu(AA)_2$)

Eq. % HDI	σ_m, psi	ϵ_m, %	E_o, psi
96	21	220	18
107	31	100	57
117	47	64	144
128	48	37	222

6b. MECHANICAL PROPERTIES OF B-2000/EXCESS TDI-BINDER CATALYST
(0.3% Pb-naphthenate)

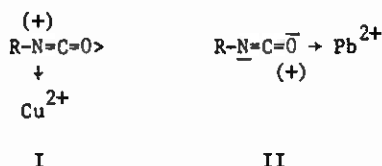| Eq. % TDI	σ_m, psi	ϵ_m, %	E_o, psi
126	55	280	48
137	80	210	96
149	138	160	130

high crosslink density ssem to be responsible. More experimentation showed that only Cu(AA)$_2$ or Cu-octoate produced cures in the presence of AP. All other catalysts failed in the presence of AP.

Table 7 lists a number of solids which were tried in the TDI/B-2000 binder, containing 30 equivalent percent excess TDI. The homopolymerization catalyst was either 0.2% Pb-naphthenate or Sn-octoate. Ammonium compounds were found to inhibit homopolymerization as brought about by the above two catalysts as is clearly indicated in the Table, while HDI-self-condensation initiated by Cu(AA)$_2$ is not greatly affected by the ammonium salts. The reason for this difference between Cu(AA)$_2$ and the divalent lead or tin compounds is not known, but may perhaps lie in the coordination between the metal ion and the isocyanate group. In the copper-isocyanate complex attachment of Cu^{2+} is probably to the N-atom of the NCO-moiety (since Cu forms strong amine complexes) while in the lead and tin-compounds association is more likely through the oxygen atom of the NCO-group, since amine complexes of the latter two metals are very weak. This hypothesis would also explain the particular efficiency of Cu(AA)$_2$ with HDI (HDI has a more basic N-atom than TDI), while it is not so active toward TDI-homopolymerization. The two activated complexes may perhaps look as follows:

$$
\begin{array}{cc}
\overset{(+)}{R-N=C=O>} & R-\underline{N}=C=\overline{O} \rightarrow Pb^{2+} \\
\downarrow & (+) \\
Cu^{2+} & \\
\\
I & II
\end{array}
$$

Obviously the two complexes will undergo different mechanisms of homopolymerization. In I, the nitrogen atom is electrophilic and nucleophilic in II. The quite different properties obtained from the two types of catalysts could perhaps be due to this difference. In addition, in structure I the N-atom will repel protons (stemming from the ammonium salt) which may block the N-atom for further reactions, while this is not so in structure II, where hydrogen bonding to the nitrogen is not impaired. Thus the inhibition of homopolymerization by ammonium perchlorate in the case of Pb^{2+} or Sn^{2+} catalyzed systems may be explained.

Attempts to overcome this inhibition of trimerization by addition of basic substances like dimethylaniline, pyridine or MgO in practical quantities (up to 1%) failed to re-establish cure, and infrared spectra of uncured batches showed the presence of unreacted NCO.

Further investigations were therefore concentrated on the HDI-Cu(AA)$_2$ combinations which is not affected by ammonium salts. A concentration series showed that within the range of 0.002 to 1% Cu(AA)$_2$ about the same

TABLE 7

EFFECT OF VARIOUS SOLIDS (LOADING 80% b.w.) ON CURE OF
B-2000/TDI COMBINATION 130 EQU. % TDI.   CATALYST EITHER
Pb-NAPHTHENATE OR Sn-OCTOATE AT 0.2% EACH

	Cure after indicated days at	
Solid	160°F	Ambient
NH_4ClO_4	Neg 3	Neg 5
Glaaa beada	Poa 1	Pos 2
$KClO_4$	Pos 1	Pos 2
LiF	Pos 1	Pos 2
$NH_4H_2PO_4$	Neg 3	Neg 10
NH_4Cl	Neg 3	Neg 10
NH_4Br	Neg 3	Neg 10
$(NH_4)_2C_2O_4$	Neg 1	Neg 10
NH_4BF_4	Neg 1	Neg 10
$MgSO_4$	Pos 1	Pos 3
MgO	Pos 1	Pos 3
$CaHPO_4$	Pos 1	Poa 3
$CaSO_4$	Pos 1	Pos 3
AlF_3	Pos 1	Pos 3
$MnCl_2$	Pos 1	Pos 3

state of cure was obtained. The properties of such propellants are extremely poor as shown in Table 8.

The next approach was to use a dual catalyst system in which one catalyst was an efficient urethane catalyst ($Fe(AA)_3$ or dibutyltindilaurate) i.e., a compound which was ineffective towards homopolymerization and the second catalyst was $Cu(AA)_2$ to trimerize residual NCO groups. Surpriaingly, the urethane catalyst inhibited trimerization, or if trimerization was affected by large quantities of $Cu(AA)_2$ or high temperature, the resulting propellant properties were no better than those achieved with $Cu(AA)_2$ alone. Figure 9 shows the infrared spectrum of a propellant extract in which an $Fe(AA)_3$-$Cu(AA)_2$ combination was employed. For comparison, the I.R. spectrum of the pure binder phase employing only the urethane catalyst (in the latter case the binder does not cure because of NCO-termination) is shown. This effect of catalyst interference in $Cu(AA)_2$-effected homopolymerization reactions was ahown by all the catalysts tested and was indpendent of the presence of AP. The other catalyats tested in combination with $Cu(AA)_2$ were: dibutyltindilaurate, $Mn(AA)_3$, $Th(AA)_4$, $UO_2(AA)_2$, $Zn(AA)_2$, Sn-octoate, Pb-octoate and $MoO_2(AA)_2$. Again, the reason for this behavior is not clear. One hint may be the observation that free acetylacetone alao inhibits the homopolymerization reaction. Thus HAA liberated from the urethane catalyst may block the action of $Cu(AA)_2$. This explanation is, however, highly conjectural.

The very poor properties of propellants containing a binder matrix crosslinked through trimerization, preclude application in practical propellants. Unless new promiaing leads are uncovered no further work on this approach is planned.

F.   THE EFFECT OF AMMONIUM PERCHLORATE ON CURE

Figure 10 showa the effect of 0.5 percent of dissolved AP in PPG* on the rate of the urethane reaction. The tests were conducted on stoichiometric PPG-BuNCO mixtures cetalyzed by 0.01% $Fe(AA)_3$. The extent of reaction was ascertained in a Beckman I.R. 9 spectrophotometer by a periodic measurement of the intensity of the carbonyl-band indicating formation of the urethane link. Apparent second order constants calculated from the alopes after 10 minutes reaction are 1.6×10^{-2} Eq^{-1} min^{-1} for the PPG-BuNCO mixture containing the dissolved AP and 2.3×10^{-2} E^{-1} min^{-1} for the control. Thus AP definitely affects the rate of cure. This has also been observed qualitatively in that urethane propellants always cure slower than unfilled binders.

In Tables 9 and 10 the effects of AP and various catalysts on isocyanates are shown for several conditions of storage. In these tests a

_____
*Of presently used prepolymers only PPG dissolves significant quantities of AP (0.5% of AP in dry PPG at room temperature) to study its effect on cure and rate of cure in homogeneous solution.

TABLE B

"TRIMERIZATION" CROSSLINKED B2000/IDP/HDI PROPELLANTS
(65% AP, 15 Al) CATALYZED BY Cu(AA)$_2$. CURED 5 DAYS AT
ROOM TEMPERATURE

	Mechanical Properties at +77°F[*]		
Equ. % HDI	σ_m, psi	ϵ, %	E_o, psi
100	31	34	140
110	50	30	280
120	68	18	620
130	68	17	680
140	70	15	735

[*]$\dot{\epsilon}$ = 0.74 in./in./min

B-2000/HDI COMBINATION CONTAINING 140 EQ. % HDI AFTER COMPLETION OF
URETHANE REACTION IN (A) PURE BINDER PHASE AND
(B) PROPELLANT

Figure 9

EFFECT OF 0.5% DISSOLVED AP ON THE RATE OF CONVERSION
IN THE PPG-BuNCO REACTION CATALYZED WITH 0.01%
$Fe(AA)_3$ AT ROOM TEMPERATURE

$k_{2(AP)} = 1.6 \times 10^{-2} E^{-1} min^{-1}$

$k_{2(control)} = 2.3 \times 10^{-2} E^{-1} min^{-1}$

PPG/AP

PPG Control

Time, Minutes

$Eq. \times 10^2$
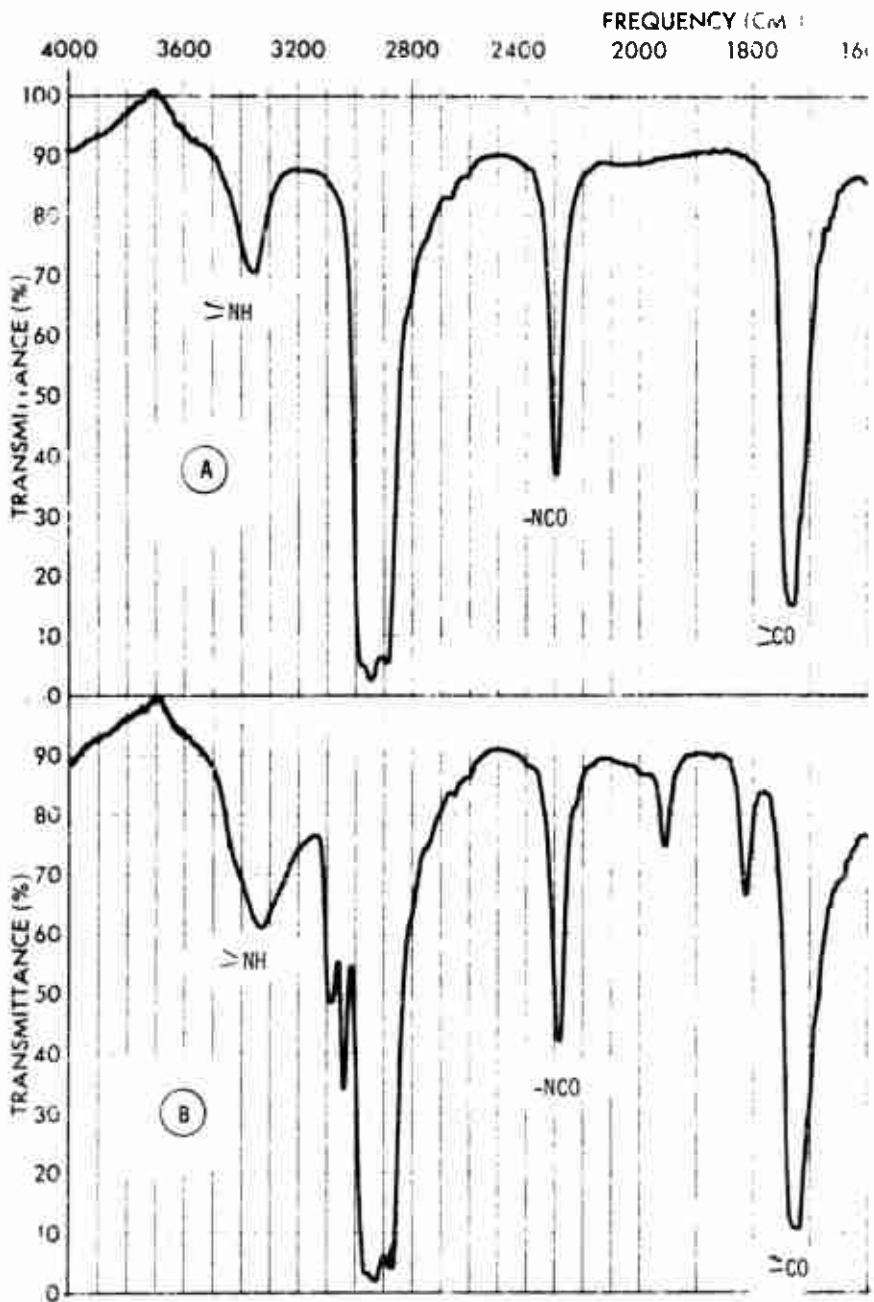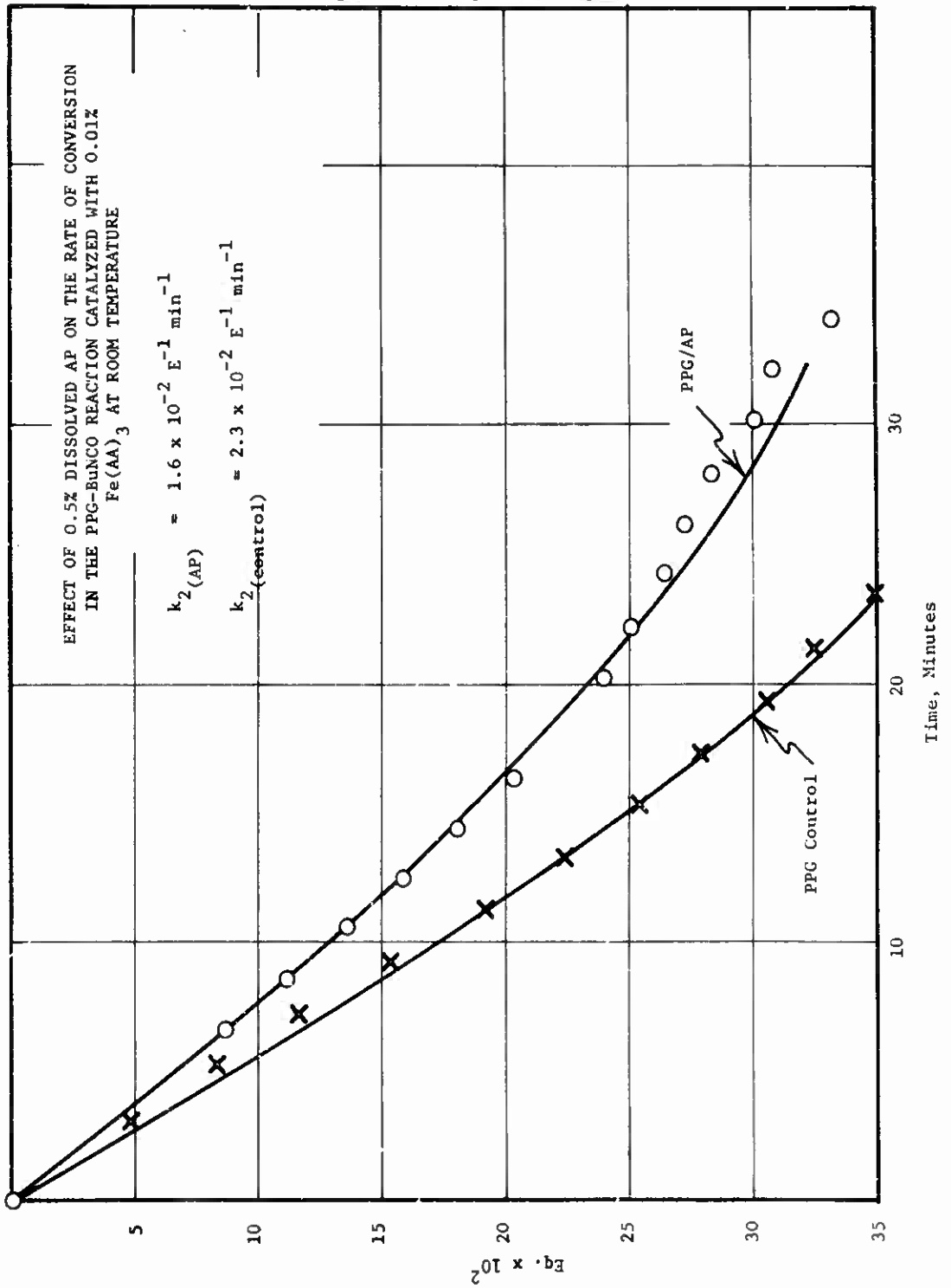
Figure 10

TABLE 9

EFFECT OF AP* AND VARIOUS CATALYSTS ON TDI-SELF-CONDENSATION. 20 HRS 150°F.

Catalyst	Per Cent of the TDI Left in[a]	
	10% Toluene Solution	80% AP + 20% Toluene Sol.
None	100	100
$Fe(AA)_3$	97	97
$Bu_2 Sn(OOCC_{11}H_{23})_2$	89	90
Pb octoate	79	91
Pb naphthenate	63	88
Sn octoate	88	89
Sn naphthenate	89	86
$Cu(AA)_2$	78	84
$UO_2(AA)_2$	91	91
$TiO(AA)_2$	82	88
$Th(AA)_4$	89	89
$VO(AA)_2$	79	77

*AP was unground type and was dried 4 days at 250°F in air.

[a]The concentration of TDI in the toluene stock solution immediately after preparation is taken to be 100%.

TABLE 10

EFFECT OF AP* AND VARIOUS CATALYSTS ON HDI-SELF-
CONDENSATION.   STORAGE 20 HRS AT 150°F.

Catalyst	Per Cent of the HDI Left in	
	10% Toluene Solution	80% AP + 20% Toluene Sol.
None	99	98
$Fe(AA)_3$	98	95
$Bu_2 Sn(OOCC_{11}H_{23})_2$	91	89
Pb-octoate	88	84
Pb-naphthenate	0^a	79
$Cu(AA)_2$	0^a	71
Sn-octoate	60	73
Zn-decanoate	80	82
$TiO(AA)_2$	64	73
$Zr(AA)_4$	78	81
$UO_2(AA)_2$	77	83
$MoO_2(AA)_2$	95	(73)
$Th(AA)_4$	83	84
$V(AA)_3$	73	77
$Mn(AA)_3$	80	80
$In(AA)_3$	80	87
Sn-oleate	60	not tested
Sn-laurate	73	not tested
Sn-naphthenate	55	not tested

*AP dried 4 days at 250°F.

[a] All HDI had gelled. Gel was not soluble in Toluene and therefore no
"NCO" was detected by I.R. Free NCO-content of gel was not determined.

10% solution of either HDI or TDI in dry toluene was added to AP in such fashion that a mixture resulted containing 80% b.w. AP and 20% solution. This approximates roughly the amount of AP to which the isocyanate in a propellant binder will be exposed. Catalysts were tested at a nominal concentration of 0.05%. The mixture was contained in Erlenmeyer flasks fitted with well greased glass stoppers to positively prevent admittance of moisture. The flasks were stored either at room temperature or 150°F for various lengths of time. Prior to testing the contents of the flasks were diluted 4:1 with toluene and the intensity of the NCO-band with that of the stock solution from which the individual splits were made. In the uncatalyzed stock solution both HDI and TDI were found to be stable, i.e., no detectable reduction of the NCO-band was observed. The precision of the tests is about $\pm$ 5% as judged from duplicate runs.

The data in Tables 9 and 10 indicate that well dried AP, in general, does not consume isocyanate. In fact, since it inhibits the homo-polymerization brought about by some of the catalysts, the concentration of unreacted NCO is often greater in the presence of AP.

Table 11 shows the effect of ambient vs 150°F storage as the HDI-toluene solution containing some representative catalysts. Other tests are planned to determine the effect of storage time, catalyst concentration and moisture content of AP on NCO-consumption.

V.   FUTURE WORK

Determine actual ratio of urethane to urea linkages formed if both water and alcoholic hydroxyls are present.

Establish structural factors of metallic catalysts which appear to favor the urethane rather than the urea or homoplymerization reactions.

With knowledge gained from above studies modify existing catalysts to minimize such side reactions.

Test modified catalysts in model systems and actual propellants.

TABLE 11

EFFECTS OF CATALYSTS ON HDI-SELF-CONDENSATION DURING STORAGE
FOR 3 DAYS AT AMBIENT AND 150°F RESPECTIVELY.   NO NH_4ClO_4 PRESENT.

| | Percent HDI Left of Original Concentration After 3 Days Storage at | |
Catalyst	Ambient	150°F
None	100	99
$Fe(AA)_3$	97	96
Bu_2 Sn-laurate	85	85
Sn-octoate	85	50
Pb-naphthenate	83	0[a]
Pb-octoate	93	61
$Cu(AA)_2$	0[a]	0[a]

[a]HDI had gelled.

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13. ABSTRACT

Numerous cure failures have been encountered in the search for catalysts which will provide ambient temperature cures for hydroxyl terminated polybutadiene propellants. These cure failures have been found to be due to side reactions which affect the stoichiometry of the reacting species and play a more dominant role than higher cure temperatures. The two most important side reactions which can lead to cure failure and/or degraded mechanical properties are the moisture-isocyanate reaction and isocyanate-homopolymerization. Both of these reactions are accelerated by metal catalysts. Tetravalent alkyltin-salts like dibutyltindilaurate and dibutyltindiacetate accelerate the moisture reaction approximately ten times more than $Fe(AA)_3$ in uncatalyzed mixtures of the reactants, while the urethane reaction is accelerated more efficiently by metal catalysts.

Divalent tin, lead and copper derivatives were found to be the strongest homopolymerization catalysts. With the exception of Cu-compounds this homopolymerization is strongly suppressed by ammonium perchlorate. A potential cure system using isocyanate trimerization as a crosslinking reaction has been abandoned because of extremely poor mechanical properties.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
1. Hydroxy Terminated Polybutadiene (HTPB)						
2. R-45						
3. Polypropylene Glycol (PPG)						
4. Hexanethylene Diisocyanate (HDI)						
5. Toluene Diisocyanate (TDI)						
6. Metal chelates						